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J.B.A. Mitchell

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Western Ontario
Department of Physics
London, Ontario, Canada N6A 3K7

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This project studied dissociative recombination of hydrogenic molecules H2(+) and H3(+). High lying Rydberg states were found to play a principle role in the determination of final products from dissociative recombination reactions essentially independent of reaction channel.

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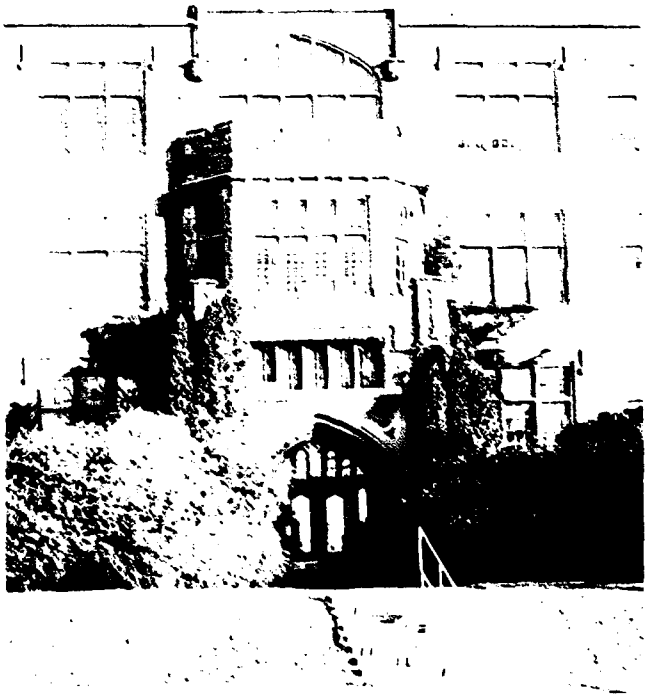

DEPARTMENT of PHYSICS

HYDROGENIC ION RECOMBINATION

J.B.A. Mitchell

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This report describes studies performed in the Merged Beams Laboratory at the University of Western Ontario on the Dissociative Recombination and Excitation of H_2^+, H_3^+, D_3^+ and HeH^+. During the last two years, the emphasis has been on measuring the identity and excitation states of the products of these recombination processes.

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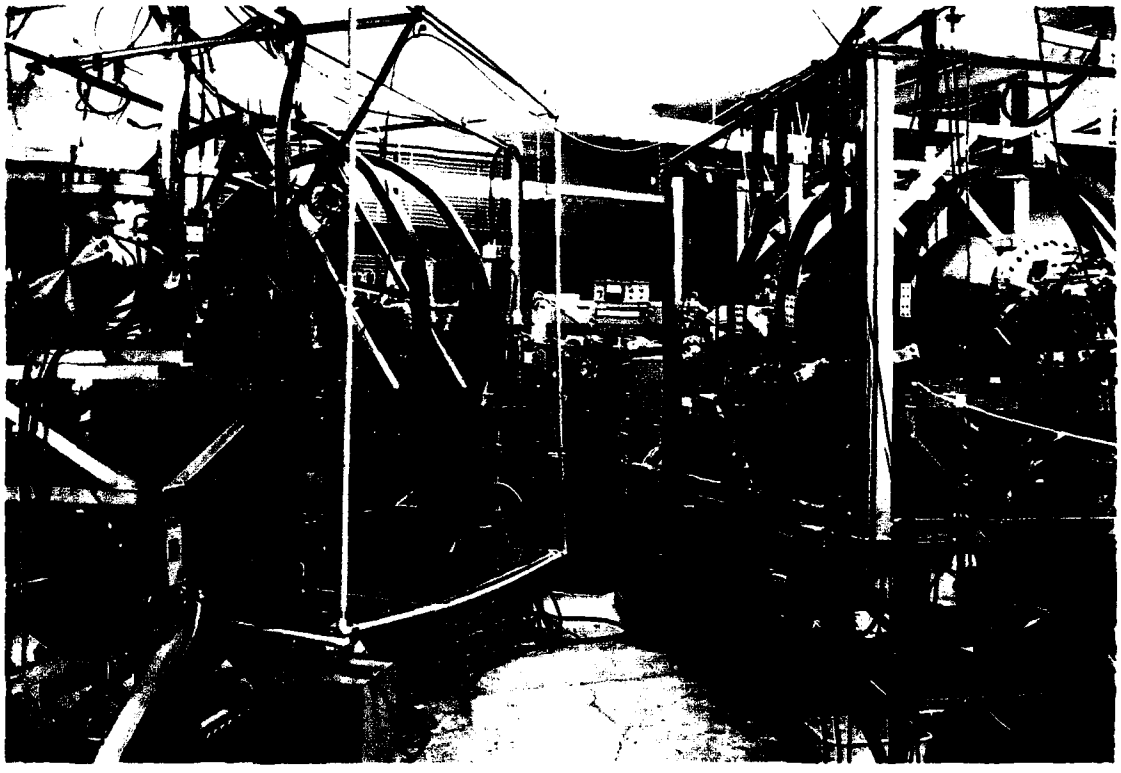

MERGED BEAM LABORATORY

DEPARTMENT OF PHYSICS

HYDROGENIC ION RECOMBINATION

Prepared for the
U.S. Air Force Office of Scientific Research

by

J.B.A. Mitchell
Associate Professor
Dept. of Physics
University of Western Ontario
London, Ontario, Canada N6A 3K7

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Principal Investigator: J.B.A. Mitchell

Primary Associates: F.B. Yousif

Graduate Student: P. Van der Donk

ABSTRACT

This is the final report of a program, sponsored by AFOSR since 1985 with the goal of understanding the dissociative recombination (DR) of the molecular ions H_2^+ and H_3^+ with electrons. These processes are important to the physics and chemistry of negative ions sources. Previous reports describing the activities carried out under this program are listed in Appendix A and Appendix B lists scientific publications arising from the program.

I. PREVIOUS STUDIES

This is the final report on a project that has been supported by US AFOSR since 1985. The aim of the project has been to understand the mechanisms underlying the dissociative recombination *DR* of hydrogenic molecules H_2^+ and H_3^+. These processes play important roles in the chemistry of volume H^- ion sources. This section will highlight some of the achievements of the project in previous years and the next section will discuss progress in this past year.

H_2^+

This is the simplest molecular ion and is amenable to accurate theoretical calculation provided the reaction mechanism is well understood. In H_2^+, the repulsive neutral state through which the recombination proceeds passes through the ion curve in the vicinity of the v=1 level, (see figure 1). This means that even for *v=0*, the direct mechanism:

$$e + H_2^+ \rightarrow H_2^{**} \rightarrow H(1s) + H(nl) \quad \ldots\ldots\ldots\ldots(1)$$

is strong. MQDT calculations, (Giusti et al., 1983, Nakashima et al. 1986) have predicted that the indirect process will give rise to window resonances in the recombination cross section since it is much weaker than the

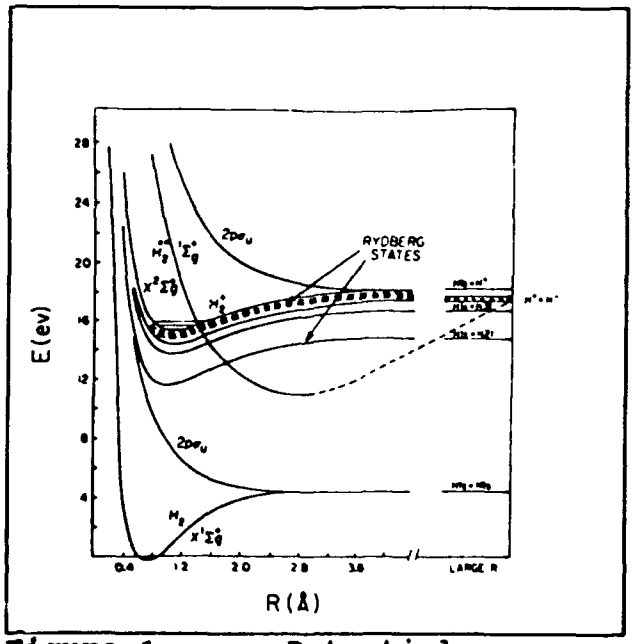

Figure 1. Potential energy curves for H_2^+ and H_2.

direct process. When the electron energy is resonant with the excitation energy to a vibrationally excited level of a bound neutral state, the wavefunction for the electron-molecular ion is localized in the bound state but the vibronic coupling to this state is weak. Thus a sharp drop in the recombination cross section is predicted to occur. Off resonance, the strong direct process dominates and the cross section is again sizable. High resolution measurements of electron-H_2^+ recombination have been performed in our laboratory. (Van der Donk, et al. 1991a, Hus et al., 1988a). A special rf trap ion source was used to produce the ions and this has been found to be capable of producing v=0 H_2^+ ions though the beam intensity^Xxs small. The results of this study are shown in figure 2. It can be seen that indeed narrow window resonances are found in the cross section. Also shown are the results of calculations of Hickman at SRI International. The agreement between theory and experiment is really quite good giving strong credence to the mechanism involving direct-indirect competition.

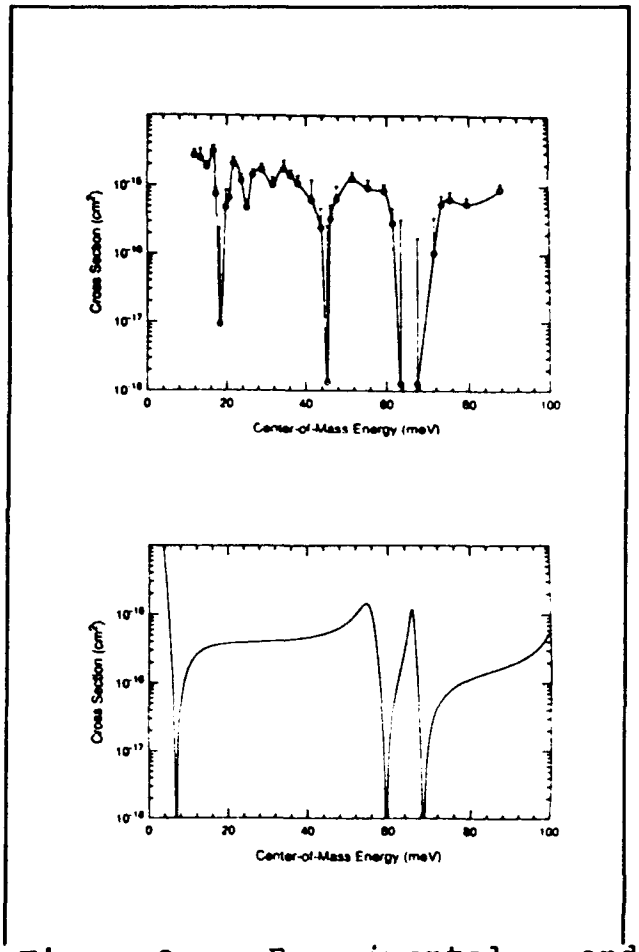

Figure 2. Experimental and theoretical DR cross sections for H_2^+(v=0). (Van der Donk et al. 1991a).

HeH^+

High resolution studies were also performed for another diatomic ion HeH^+. (Yousif and Mitchell, 1989) (Figure 3). This measurement is very significant for HeH^+ does not have any intersecting neutral state and it had always been assumed that its dissociative recombination would be negligible. In fact it is quite large, at least at low energies, the corresponding rate coefficient being about $1x10^{-8}$ cm^3s^{-1} at room temperature.

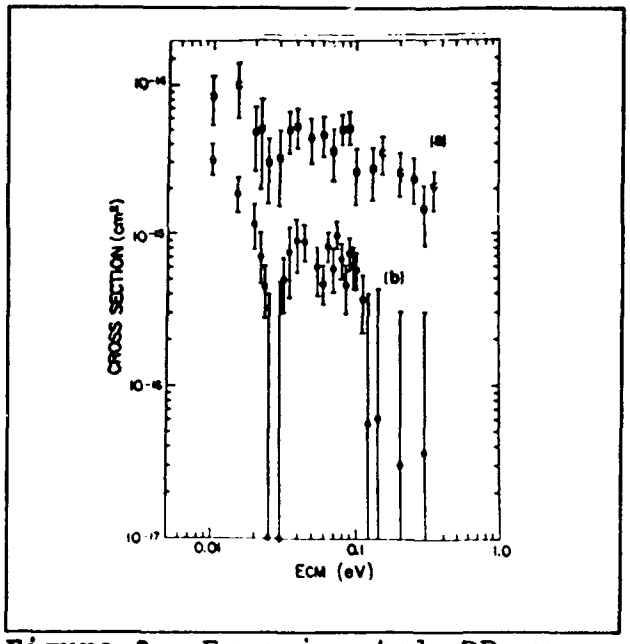

Figure 3. Experimental DR cross sections for HeH^+. (Yousif and Mitchell, 1989).

H_3^+

This ion is usually the most abundant ionic species in molecular hydrogen plasmas at elevated pressures and its recombination rate is a quantity of great importance. It has also been a source of controversy during the 80's. Adams et al. (1983) performed a FALP study of this process and found the recombination rate to be extremely small. ($<2 \times 10^{-8}$ cm^3s^{-1}). They claimed that their measurement referred to ground vibrational state ions and that their result was justified by the non-optimal position of the curve crossing between H_3^+ and the neutral dissociating H_3^{**} state. (Fig. 4.). Cross sections for H_3^+ recombination were measured as a function of energy and internal energy using the merged beams technique, (Hus et al. 1988b). (Figure 5). It was found that as *v*

was lowered, the 300K rate coefficient did indeed decrease to a value of about 2 x 10^{-8} cm^3s^{-1} for *v=0*. Unfortunately, by the time this measurement was made, Adams et al. had revised their rate coefficient estimate down to <1 x 10^{-11} cm^3s^{-1}. Meanwhile, Amano in Ottawa had found a value for α(v=0) of 1.8 x 10^{-7} cm^3s^{-1}! The principal investigator spent six months in France in 1990, working in the Flowing Afterglow laboratory of B.R. Rowe. While there, he became aware that the H_3^+ de-excitation rate used by proponents of the FALP technique were too high by up to two orders of magnitude for low *v* states. The implication of this is that the FALP measurement of Adams et al. had actually used vibrationally excited H_3^+ ions and so the theoretical justification for these measurements was in fact lacking. FALP measurements performed in France on ground state ions (Canosa et al. 1992) were found to agree with the results of Amano. This is about a factor of five higher than the merged beams result. More will be said about this in the next section. Mitchell came up with a proposed mechanism to explain the high recombination rate in the absence of a strong direct mechanism. This involves a transition to a high v, low n neutral rydberg state which is subsequently predissociated by the ground state. Such a mechanism could also explain the HeH^+

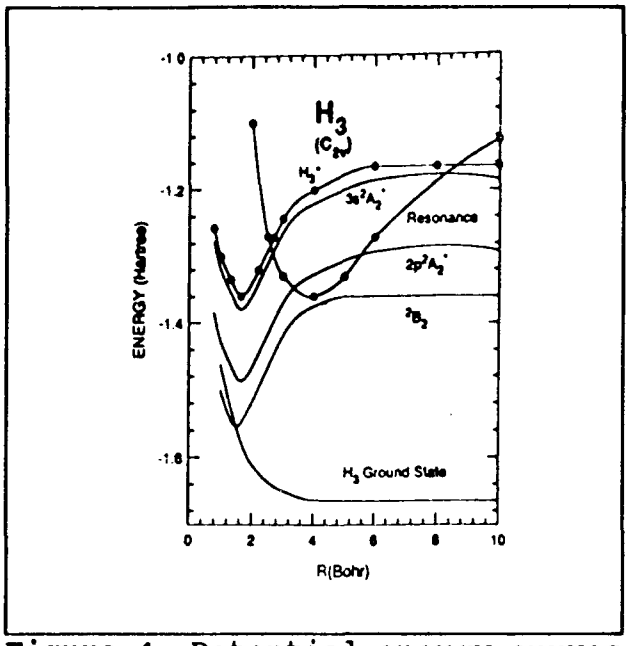

Figure 4. Potential energy curves for H_3 and H_3^+. (Michels and Hobbs, 1984).

recombination. Independent experimental evidence for such transitions has comes from high Rydberg studies of Bordas and Helm (1991).

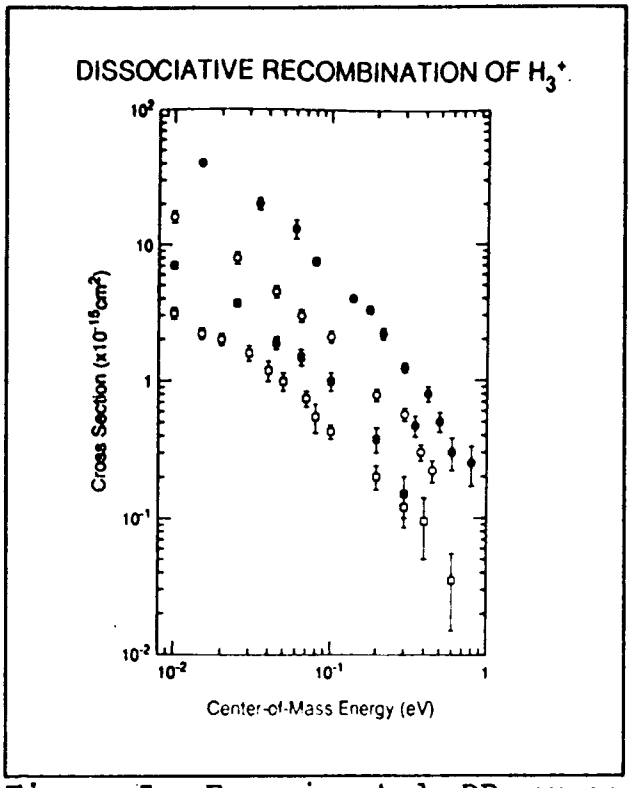

Figure 5. Experimental DR cross sections for H_3^+. ● RF source □ Trap source low press., ■Trap source high press., ▯Trap source low extraction.

H_3^+ Branching Ratios

A technique for determining the number of products arising from dissociative recombination was developed in this laboratory. This technique is described in detail elsewhere. (Forand et al. 1985). The H_3^+ DR can be represented as follows:

$$e + H_3^+ \rightarrow H + H + H \quad \text{.....(2a)}$$

$$\rightarrow H_2 + H \quad \text{.....(2b)}$$

$$\rightarrow H_3^* \quad \text{.....(2c)}$$

It was found for v=0 ions and a collision energy of 10 meV, channels 2a and 2b contributed 52% and 40% respectively, while channel 2c accounted for as much as 8% of the total recombination cross section, (Mitchell and Yousif, 1989). This was very surprising for in order to reach the detector, the H_3^* molecules would have to have lifetimes of at least 10^{-7}s.

D_3^+

This ion has been studied and it has been found that at low electron energy, the cross section is about the same as that for H_3^+, (Van der Donk et al. 1991b) (Figure 6). Earlier studies had found that the D_3^+ recombination was slower than H_3^+ recombination. This observation can be explained however. The earlier measurements were performed on excited ions. When D_3^+ ions are initially formed, they have higher vibrational states populated than H_3^+. These high states however have fast de-excitation rates and so are rapidly quenched to the ground state. H_3^+ is formed with a higher percentage of low v states populated. These have slow de-excitation rates. This means that the D_3^+ ions actually had a lower vibrational state distribution than the H_3^+ ions. Since the measured σ_{DR} is found to decrease with decreasing v, this explains the lower D_3^+ DR cross section in the earlier studies.

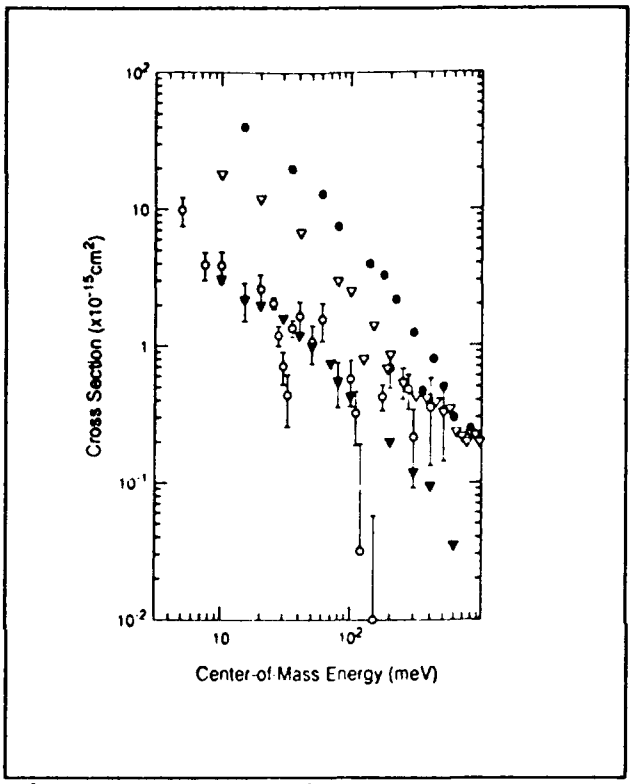

Figure 6. Experimental DR cross sections for D_3^+, ○ Trap source, △ rf source and H_3^+ ▼ trap source, ● rf source. (van der Donk et al. 1991b)

Dissociative Excitation

During the course of these studies, measurements of the dissociative excitation *DE* reactions:

$$e + HeH^+ \rightarrow H + He^+ + e \quad \text{.....(3)}$$

$$e + H_3^+ \rightarrow H + H_2^+ + e \quad \text{.....(4)}$$

$$e + D_3^+ \rightarrow D + D_2^+ + e \quad \text{.....(5)}$$

were performed in order to determine the internal energy of the ions. It was found that these reactions displayed sharp resonant structures. (Van der Donk, 1991,b, Yousif et al, 1991a) (See figures 7 and 8). This is surprising since theoretical studies of such processes have predicted that the cross sections should be smoothly varying. This subject is still under investigation and a new crossed-beams apparatus dedicated to this subject is nearing completion.

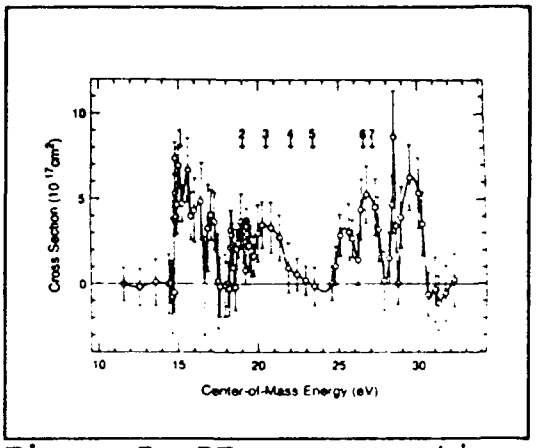

Figure 7. DE cross sections for $H_3^+(v=0)$. (Yousif et al. 1991a).

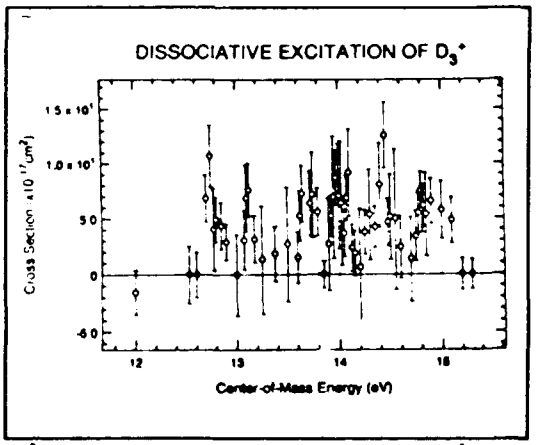

Figure 8. DE Cross sections for $D_3^+(v=0)$. (Van der Donk et al. 1991b).

Stimulated Radiative Recombination Studies

This part of the program has actually been supported by a separate USAF grant but it should be mentioned here as the results pertain directly to this project. Yousif et al. (1991a) have found that radiative recombination to the n=11 and n=12 states of atomic hydrogen can be stimulated by irradiating the electron-ion interaction region by 10.6 μm laser light. Thus the process is:

$$h\nu + e + H^{+} \rightarrow H(nl) + 2h\nu \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The results are shown in figure 9. What is especially significant to the DR program is the fact that the resonances measured at 5.33 and 23.3 mev had widths of 0.5 and 1.2 mev respectively. This dramatically illustrates the very high energy resolution and low energy capabilities of the merged beams technique.

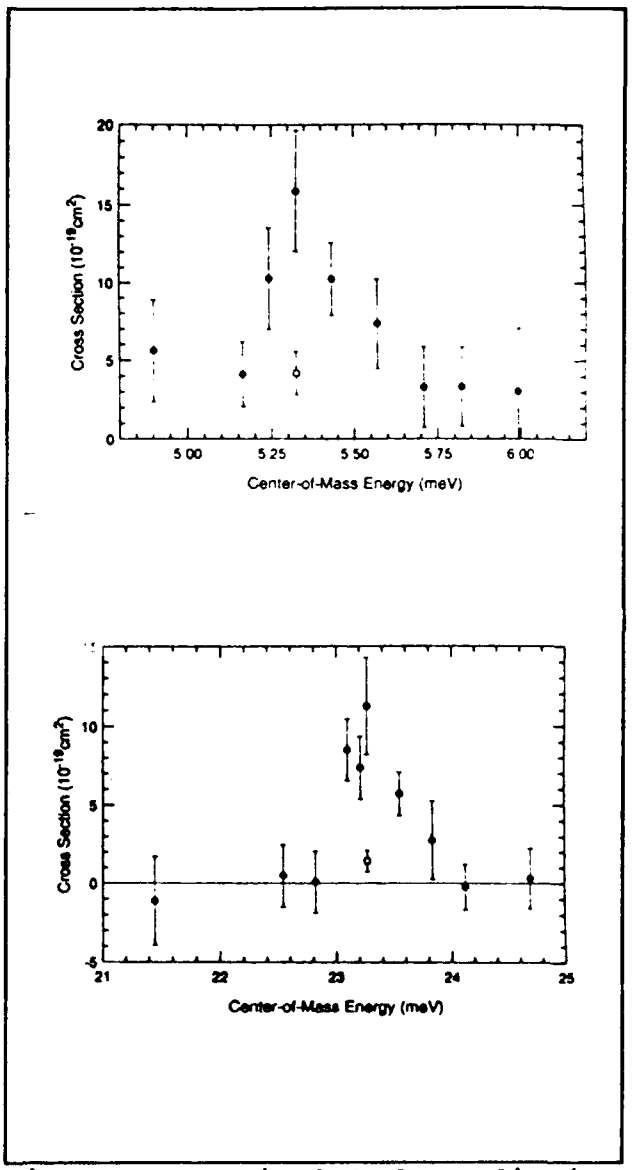

Figure 9. Stimulated radiative recombination to the n=11 and n=12 states of H. (Yousif et al. 1991).

II. RECENT STUDIES

Most of the studies described above were concerned with the total recombination cross section. They concentrated on the electron capture part of the reaction. More recently, the emphasis of the program has been on determining the excitation states and identities of the final products of the recombination. Part of the justification for this study was to identify the reason for the factor of five discrepancy between the merged beams results for H_3^+ DR and the FALP results.

It should be pointed out firstly that the merged beam result for excited state H_3^+ ions agrees with the results of Amano (1990), Leu et al (1973) and the Rennes FALP results of Canosa et al. (1992). The discrepancy only arises when the ions are cooled down for then the merged beams results are seen to decrease while the results of other measurements appear to be independent of internal energy. In the merged beams experiments of Hus et al., the H_3^+ ions were produced using an rf trap ion source and it was found that $v=0$ ions could be produced by reducing the extraction potential of the source to a low value. In order to check that the observed cross section decrease is not a consequence of ion source operating conditions, a completely different ion source was installed in the Van de Graaff accelerator which acts as the injector into the merged beams experiment. This source was an rf source, similar to that used for our early studies of H_3^+ recombination (Auerbach et al. 1977, Mitchell et al. 1983 and Mitchell et al. 1985) but with a narrow exit canal so that the source can be operated at elevated

pressures.

The cross section for H_3^+ DR at 10 meV measured as a function of source pressure is shown in figure 10. It can be seen that the DR cross section decreases with increasing pressure reaching a value consistent with that obtained using the ion trap source at low extraction. Increasing the pressure leads to a cooling down of the vibrational temperature of the ions due to the reaction:

$$H_3^+(v) + H_2(v=0) \rightarrow H_3^+(v=0) + H_2(v) \quad ...(7)$$

Thus the decrease in the cross section observed in the experiment of Hus et al., and obtained by altering the extraction potential of the trap ion source, is reproducible by altering the pressure in the rf source. It should also be mentioned that the Hus et al. results were taken using the old MEIBE I apparatus in the laboratory. The new measurements have been taken using the new MEIBE II apparatus. These two machines are shown in the frontispiece to this report. Figure 10 shows that when the pressure is raised sufficiently, a re-excitation of the ions occurs. This may be due to excitation of the ions in the extraction region. Raising the pressure in the source also implies raising the pressure in the region where the ions are being accelerated and they may

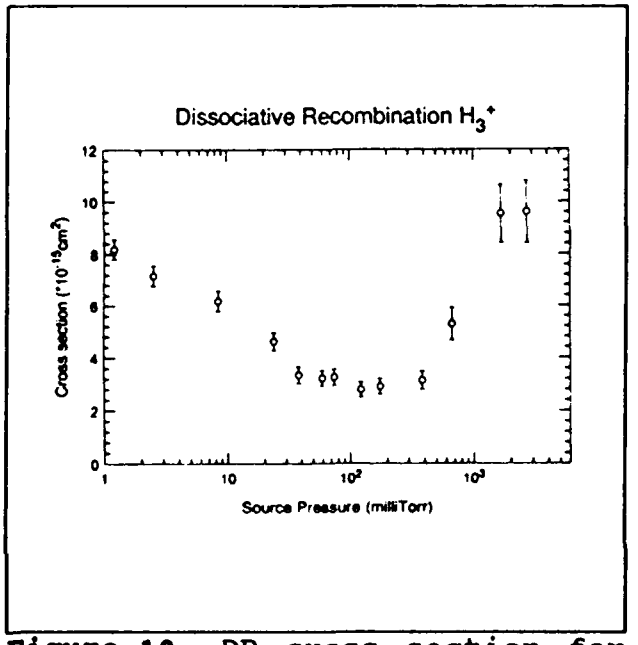

Figure 10. DR cross section for H_3^+ at 10 meV as a function of source pressure.

make inelastic collisions in this region resulting in an increase in their internal energy.

The experiment just described is a strong justification that there is some difference occurring in the dissociative recombination reaction as the vibrational state of the ions is reduced. Indeed, this must be so for, at elevated vibrational levels, the ion can recombine via direct dissociation through the neutral H_3^{**} state shown in figure 4. At low *v* however, this channel is not available and another recombination mechanism must be invoked. It is surprising therefore that the Rennes FALP and Amano's experiments both find that the rate coefficient varies little with decreasing *v*.

One possible explanation for the lower cross section measured by the merged beam method is that the recombination process proceeds via the formation of long lived rydberg states of H_3^* which are perhaps destroyed in the high electric fields used to separate the ions from the neutral products. In order to examine this possibility, a number of experiments have been performed in which the final states of ions arising from DR have been measured.

H_2^+

Dunn and Co-workers (Phaneuf et al. 1975, Vogler and Dunn, 1975) measured the cross sections for the reactions:

$$e + H_2^+ \rightarrow H(1s) + H(2s) \quad .....(8)$$

and

$$e + H_2^+ \rightarrow H(1s) + H(n=4) \quad .....(9)$$

using a crossed beams experiments. No attempts were made in these experiments to produce ground vibrational state ions. The excited

vibrational states of H_2^+ have very long lifetimes (10^6s) and indeed, Dunn (1968) had determined that the H_2^+ ions produced from his ion source had a vibrational state distribution that was rather similar to that predicted by Franck-Condon ionizing transitions. Dunn found that each of these two dissociative recombination channels accounted for about 10% of the total recombination cross section,

$$e + H_2^+(v) \rightarrow H(1s) + H(nl) \quad \ldots\ldots\ldots\ldots (10)$$

measured by Peart and Dolder (1974a).

It is intriguing to ask where the other 80% of the reaction cross section goes? For H_2^+ ions in their vibrational ground state, the only open dissociative channel that can be reached via the direct process is H(1s) + H(n=2), (see figure 1). For ions with a Franck-Condon distribution of vibrational states, all final states H(1s) + H(nl) plus the ion-pair channel $H^+ + H^-$ are open. Peart and Dolder (1975) showed that the latter channel accounts for about 0.1% of the total cross section.

We have two projects in place to study the final excitation states of the neutrals. The first involves the use of a time and position sensitive detector and is intended to examine the formation of low rydberg state hydrogen atoms. This detector has been described in an earlier report (Mitchell, 1989). Steady progress has been made in the implementation of this detector but as yet the resolution obtained has been insufficient to distinguish between final channels.

The second project utilizes the field ionization detection scheme which was installed in the MEIBE II apparatus to detect the

products of the stimulated radiative recombination process. Two field ionization detectors are installed in series following the interaction region as shown in figure 11. These detectors each consist of an in-line field ionizer capable of producing an axial electric field of 150KV/cm, an electrostatic ion deflector assembly and a surface barrier detector. They can each detect neutral species with principal quantum number states n>10. States with n≥20 are field ionized in the ion analyzer following the interaction region and so do not enter the field ionizers.

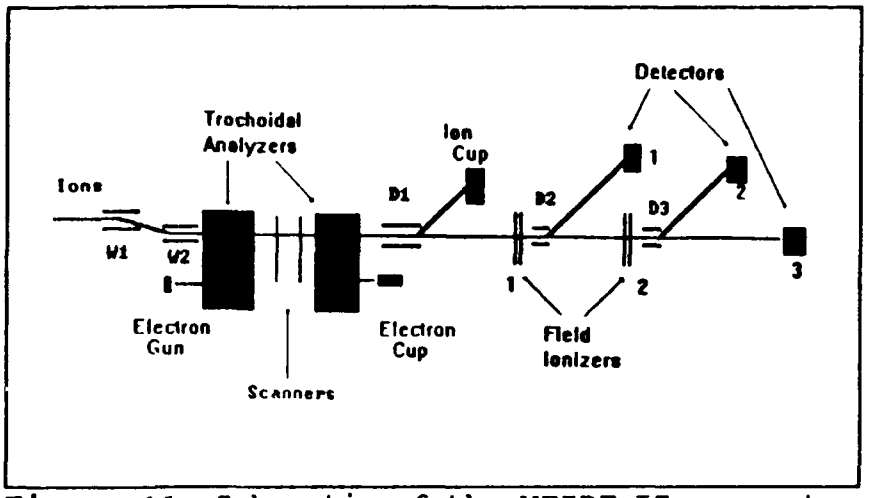

Figure 11. Schematic of the MEIBE II apparatus showing the field ionizers.

Using these devices, we have been able to measure the DR channel:

$$e + H_2^+ \rightarrow H(1s) + H(10<n<20) \quad .....(11)$$

The cross section for this channel is shown in figure 12 together with the cross section for:

$$e + H_2^+ \rightarrow H(1s) + H(n\leq 10) \quad .....(12)$$

Note that this latter channel is not exactly the total DR process

$$e + H_2^+ \rightarrow H(1s) + H(nl) \quad .....(13)$$

since states higher than n=10 are field ionized and not detected but the difference is small. It can be seen that the cross section

for channel (11) accounts for about 10% of the cross section for channel (12). Also shown in figure 12 is the cross section for the reaction channel:

$$e + H_2^+ \rightarrow H_2^* \quad \ldots\ldots\ldots\ldots\ldots\ldots (14)$$

It is surprising that any signal due to this channel is seen at all, for the direct process is strong in H_2^+. Indeed, the evidence shown in figure 2 indicates that the direct process is much stronger than the indirect mechanism in which H_2^* Rydberg states are formed. What is even more surprising however is the fact that the H_2^* states seen must have lifetimes in excess of 10^{-7} s in order to reach the detector. The standard indirect process is usually thought of as proceeding through short lived autoionizing rydberg states which are quickly predissociated by the repulsive H_2^{**} state:

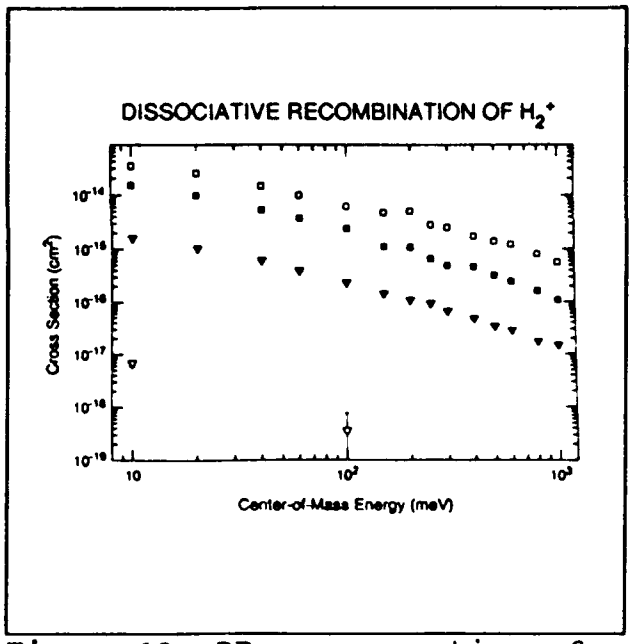

Figure 12. DR cross sections for H_2^+ to form ■ H(n<10), ▼ H(10<n<20), ▽ H_2(10<n<20). □ DE cross section.

$$e + H_2^+ \rightarrow H_2^R \rightarrow H_2^{**} \rightarrow H(1s) + H(nl) \quad \ldots\ldots\ldots (15)$$

H_3^+

The same technique has been used for the products of H_3^+ recombination. In this case, hydrogen atom products in Rydberg states with n>10 can only be formed from ions in vibrational states with v≥11. Indeed it was found that the proton signal measured after the field ionizer rapidly disappeared as the source pressure

was increased, in other words, as the vibrational state distribution of the ions in the beam was driven to lower *v* values. Again however, signals arising from H_3^* molecules were found and that this signal increased in intensity as the source pressure was raised. This is shown in figure 13.

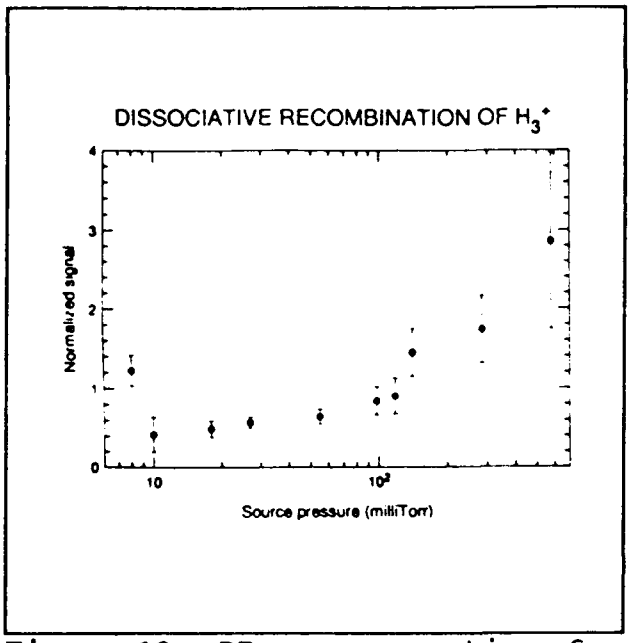

Figure 13. DR cross section for H_3^+ to form $H_3^*(10<n<20)$ as a function of source pressure.

Ion Pair Production.

One possible exit channel for the dissociative recombination of H_3^+, is the ion-pair channel, i.e.:

$$e + H_3^+(v=0) \rightarrow H_2^+ + H^- \quad \text{.....(16)}$$

This channel is endothermic by 5.3 eV for ions in the *v=0* state. This means that the process exhibits a threshold as the electron energy is increased. Peart, Forrest and Dolder (1979) have already measured the cross section for this process and their results are shown in figure (14). These measurements used vibrationally excited ions and it can be seen that the threshold appears at 2-3 eV. This shows that the ions used had about 2.3-3.3 eV of internal excitation. Our results are also shown in figure (15) and it can be seen that they exhibit a threshold between 5.0

and 5.5 eV. This means that the ions are in their vibrational ground state.

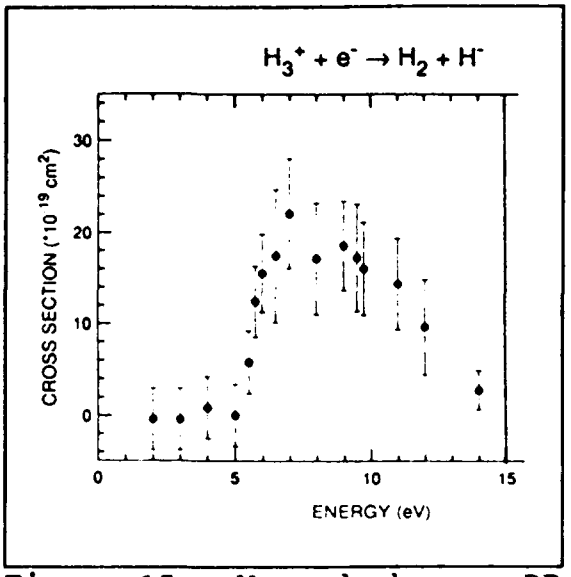

Figure 15. Merged beams DR cross sections for $H_3^+(v=0)$ to form $H_2^+ + H^-$.

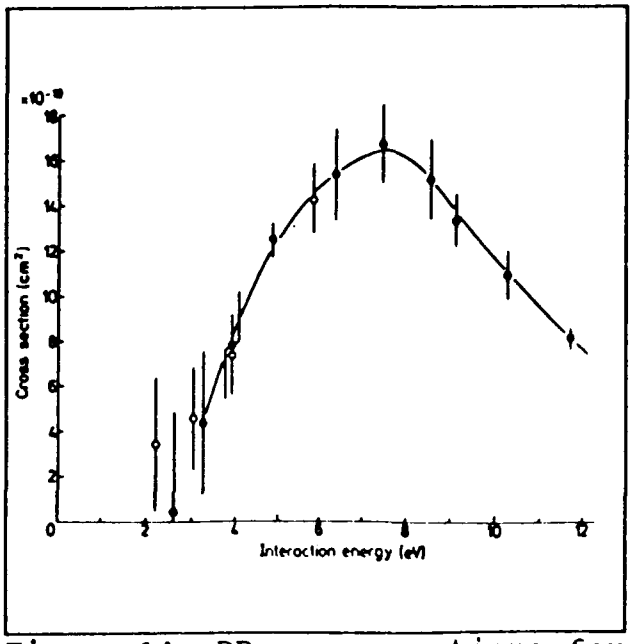

Figure 14. DR cross sections for H_3^+ to form $H_2^+ + H^-$. (From Peart et. al. 1979).

The most significant feature of these results is the fact that our data agree very well with that of Peart et al. (1979). As mentioned earlier, the results that we obtained with excited ions agree well with those of Canosa et al. (1992), Amano (1990) and Leu et al. (1973). Figure 16 shows the results of Hus et al. (1988), Leu et al. (1973), Peart and Dolder (1974b) and Auerbach et al. (1977). The latter represents some early data taken with our merged beams

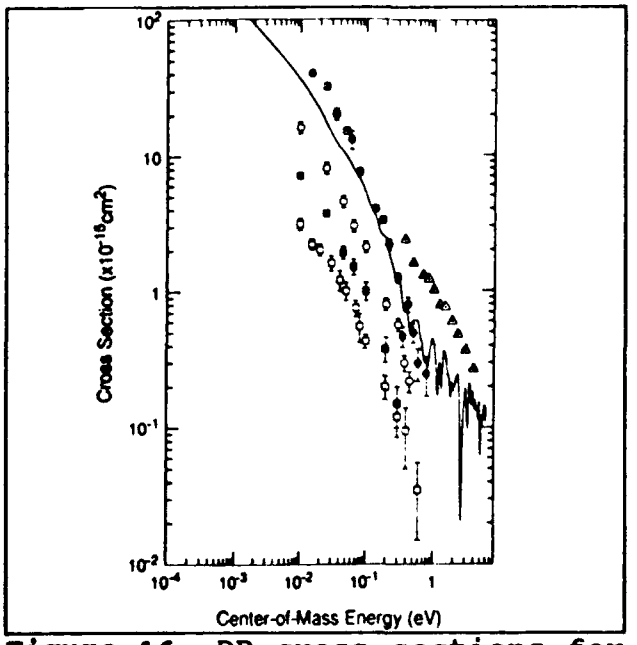

Figure 16. DR cross sections for H_3^+ showing data of Hus et al. and that of □ Leu et al. (1973) and of ▵ Peart and Dolder (1974b).

apparatus and is included here as it extended up to 6 eV and so is directly comparable to that of Peart and Dolder. It can be seen that the data of Hus et al. agrees closely with that of Auerbach et al. especially in the range from 0.1 to 0.8 eV. The data of Peart and Dolder is considerably higher in this range but the trend is for the two results to converge at higher energies. The steep increase in the slope of dissociative recombination cross sections above 0.1 eV has been observed in this laboratory for many other polyatomic ions. (McGowan et al. 1979, McGowan and Mitchell, 1984). Diatomic species, on the other hand, have been observed to display a constant E^{-1} energy dependance throughout the entire range of observation. Auerbach et al. was the only measurement, made by us, which extended the energy range up to a few eV and the data suggests that the change of slope is in fact due to the recombination signals being depleted in this energy range. This has been interpreted as being due to competition from vibrational excitation processes but it could in fact be interpreted in terms of Rydberg formation and destruction by field ionization. If this was the case and if the experimental arrangement of Peart and Dolder was such as to preclude Rydberg state destruction, then this would imply that in fact, barring field ionization effects, the data of Hus et al., Auerbach et al. and Peart and Dolder would all agree.

The dissociative recombination process for H_2^+ and H_3^+, leading to the formation of neutral products must ultimately involve transitions from the initial doubly excited states to neutral Rydberg states for the doubly excited states have ion-pair

asymptotes.

In the case of $H_2^+ + H^-$ formation, this procedes through a direct transition to the H_3^{**} state and so does not involve Rydberg state transitions. It is not surprising therefore that we would not see any field ionization effects in this case and that good agreement would be obtained with the Peart and Dolder data.

In summary then, the data presented here points to the strong involvement of high lying Rydberg states in recombination and any theoretical model for this process must include the influence of these states. This is particularly important for models whose aim is to predict the final products of dissociative recombination.

REFERENCES

Adams, N.G., Smith, D. and Alge, E. (1983) J. Chem. Phys. **81**, 1778.

Amano, T. (1988) Astrophys. J. **329**, L121.

Amano, T. (1990) J. Chem. Phys. **92**,6492.

Auerbach, D., Cacak, R., Caudano, R., Gaily, T.D., Keyser, C.J., McGowan, J.Wm., Mitchell, J.B.A. and Wilk, S.F.J. (1977) J. Phys. B. **10**, 3797.

Bordas, C. and Helm, H. (1991) Phys. Rev. A. **44**, 1817.

Canosa, A., Gomet, J.C., Rowe, B.R., Mitchell, J.B.A. and Queffelec, J.L. (1992) J. Chem. Phys. (In press).

Dunn, G.H. (1968) Phys. Rev. **172**, 1.

Forand, J.L., Mitchell, J.B.A. and McGowan, J.Wm. (1985) J. Phys. E. **18**, 623.

Giusti-Suzor, A., Bardsley, J.N. and Derkits (1983) Phys. Rev. A. **28**, 682.

Hus, H., Yousif, F.B., Noren, C., Sen, A. and Mitchell, J.B.A. (1988) Phys. Rev. Lett. **60**, 1006.

Hus, H., Yousif, F.B., Sen, A., and Mitchell, J.B.A. (1988) Phys. Rev. A. **38**, 658.

Leu, M.T., Biondi, M.A. and Johnsen, R. (1973) Phys. Rev. A. **8**, 413.

McGowan, J.B.A., Mul, P.M., D'Angelo, V.S., Mitchell, J.B.A., Defrance, P. and Froelich, H.R. (1979) Phys. Rev. Lett. **42**, 373.

McGowan, J.Wm. and Mitchell, J.B.A. (1984) in *Electron-Molecule Interactions and Their Applications, Vol. II* ed. L.G. Christophorou (Academic Press, Orlando)

Mitchell, J.B.A., Forand, J.L., Ng, C.T., Levac, D.P., Mitchell,

R.E., Mul, P.M., Claeys, W., Sen, A. and McGowan, J.Wm. (1983) Phys. Rev. Lett. **51**, 885.

Mitchell, J.B.A., Forand, J.L., Ng., C.T., Janssen, R. and McGowan, J.Wm. (1985) J. Phys. B. **17**, L909.

Mitchell J.B.A. *Merged Beam Studies into the Mechanisms of Hydrogen Molecular Ion Recombination* Report to AFOSR, 30 Sep 1989.

Mitchell, J.B.A. and Yousif, F.B. (1989) in *Microwave and Particle Beam Sources and Directed Energy Concepts, Vol 1061* ed H.E. Brandt, (Opt. Soc. Am) p.61.

Nakashima,K., Takagi, H., and Nakamura, H. (1986) J. Chem. Phys. **86**, 726.

Peart, B. and Dolder, K.T. (1974a) J. Phys. B. 7, 236.

Peart, B. and Dolder, K.T. (1974b) J. Phys. B. **7**, 1948.

Peart, B. and Dolder, K.T. (1975) J. Phys. B. **8**, 1570.

Peart, B., Forrest, R.A. and Dolder, K.T. (1979) J. Phys. B. **12**, 3441.

Phaneuf, R., Crandall, D. and Dunn, G.H. (1975) Phys. Rev. A. **11**, 528.

Van der Donk, P., Yousif, F.B., Mitchell, J.B.A. and Hickman, A.P. (1991a) Phys. Rev. Lett. **67**, 42.

Van der Donk, P., Yousif, F.B. and Mitchell, J.B.A. (1991b) Phys. Rev. A. **43**, 5971.

Vogler, M. and Dunn, G.H. (1975) Phys. Rev. A. **11**, 1983.

Yousif, F.B. and Mitchell, J.B.A. (1989) Phys. Rev. A.

Yousif, F.B., Van der Donk, P.J.T., Orakzai, M. and Mitchell, J.B.A. (1991a) Phys. Rev. A. **44**, 5653.

Yousif, F.B., Van der Donk, P., Kucherovsky, Z., Reis, J., Brannen, E., Mitchell, J.B.A. and Morgan, T.J. (1991b) Phys. Rev. Lett. **67**, 26.

APPENDIX A.

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1. Merged Beam Studies of the Dissociative Recombination of H_3^+ Ions with Low Internal Energy.
AFOSR-85-0279 $19,794. 1 Sep 85-30 Mar 86.
2. Merged Beam Studies of the Dissociative Recombination of H_3^+ and H_2^+.
AFOSR-86-0234 $34,836 1 Sep 86- 30 August 87
3. Merged Beam Studies into the Mechanisms of Hydrogen Molecular Ion Recombination.
AFOSR-87-0365 $61,844 1 Sep 87-31 Aug 89

4. Dissociative Recombination: Theory, experiment and Application
AFOSR-88-0173 $10,500 1 May 88-30 Sep 89. (Conference Grant).

5. Investigations into the Mechanisms of Hydrogenic Ion Recombination.
AFOSR 90-0042 $69,692 30 Oct 89-31 Oct 1991

APPENDIX B.
Papers published directly and indirectly resulting from the grants listed in Appendix A.

1. The Dissociative recombination and excitation of D_3^+.
   P. Van der Donk, F.B. Yousif and J.B.A. Mitchell
   Phys. Rev. A. **43**, 5971, 1991.

2. Dissociative recombination of H_2^+. Comparison of theory and experiment.
   P. Van der Donk, F.B. Yousif, J.B.A. Mitchell and A.P. Hickman
   Phys. Rev. Lett. **67**, 42, 1991.

3. The Dissociative excitation and recombination of H_3^+.
   F.B. Yousif, P. Van der Donk, M. Orakzai and J.B.A. Mitchell
   Phys. Rev. A. **44**, 5653, 1991.

4. Rate coefficients for $N_2^+(v)$ dissociative recombination.
   D.R. Bates and J.B.A. Mitchell
   Planet. Space Sc. **39**, 1297, 1991.

5. The Excitation state of Ions in Afterglow Experiments
   J.B.A. Mitchell and B.R. Rowe
   (In preparation).

6. Flowing afterglow studies of H_3^+ recombination.
   A. Canosa, B.R. Rowe, J.C. Gomet, J.L. Queffelec and J.B.A. Mitchell
   J. Chem. Phys. (In press).

7. A further study of HCO^+ dissociative recombination.
   B.R. Rowe, J.C. Gomet, A. Canosa, C. Rebrion and J.B.A. Mitchell
   J. Chem. Phys. (In press).

8. New measurements of H_3^+ and HCO^+ dissociative recombination rate coefficients.
   A. Canosa, B.R. Rowe, J.B.A. Mitchell, J.C. Gomet and C. Rebrion.
   Astron. Astrophys. **248**, L19, 1991.

9. New experiments on H_3^+ recombination.
   J.B.A. Mitchell and B.R. Rowe
   Proceedings of the 3rd US/Mexico Symposium on Atomic Collisions. (eds. C. Cisneros and T.J. Morgan) World Scientific, Singapore, 1991.

10. Electron-ion recombination.
    J.B.A. Mitchell
    in Ion impact phenomena (Ed. D. Mathur). Springer-Verlag, Berlin, 1991. p. 275.

11. Recent developments in molecular ion recombination research
J.B.A. Mitchell
in Electron and Atomic Collisions (Ed. A. Dalgarno, R.S. Freund, M.S. Lubell and T.B. Lucatorto) AIP Conference Proceedings No. 205, New York, 1990, p. 404.

12. The dissociative recombination of molecular ions.
J.B.A. Mitchell
Physics Reports **186**, 215, 1990.

13. Dissociative Recombination: Theory, Experiment and Applications.
J.B.A. Mitchell and S.L. Guberman
World Scientific, Singapore, 1989.

14. The dissociative recombination and excitation of N_2^+.
C. Noren, F.B. Yousif and J.B.A. Mitchell.
J. Chem. Soc. Faraday Trans. II **85**, 1697, 1989.

15. Recombination and excitation of HeH^+.
F.B. Yousif and J.B.A. Mitchell
Phys. Rev.A. **40**, 4318, 1989.

16. Molecular ion recombination: Branching ratio measurements.
J.B.A. Mitchell and F.B. Yousif
Microwave and Particle Beam Sources. (ed. H.E. Brandt). SPIE publication. Vol 1061. Bellingham, WA, 1989, p. 536.

17. Cluster ions and the meteor head echo.
J. Jones and J.B.A. Mitchell
Monthly Not. Roy. Astr. Soc. **232**, 771, 1988.

18. Merged beam studies of the dissociative recombination of H_3^+ ions with low internal energy.
H. Hus, F.B. Yousif, A. Sen and J.B.A. Mitchell
Phys. Rev. A. **38**, 658, 1988.

19. Merged beam studies of the dissociative recombination of H_2^+ ions in low vibrational states.
H. Hus, F.B. Yousif, C. Noren, A. Sen and J.B.A. Mitchell.
Phys. Rev. Lett. **60**, 1006, 1988.

20. Production of low vibrational state H_2^+ ions for collision studies.
A. Sen, J.Wm. McGowan and J.B.A. Mitchell
J. Phys. B. **20**, 1509, 1987.

21. The role of H_3^+ ions in negative ion sources.
J.B.A. Mitchell and W.G. Graham.
Production and Neutralization of Negative Ions and Beams. 4th Int. Conf. Brrokhaven, 1986. AIP Conf. Proc No. 158. NY, 1987., p.39.

22. Electron-ion collision processes relevant to H^- ion sources. Production and Neutralization of Negative Ions and Beams. 4th Int. Conf. Brrokhaven, 1986. AIP Conf. Proc. No. 158, NY 1987, p.26.

23. Production of H_3^+ ions with low internal energy for studies of dissociative recombination.
A. Sen and J.B.A. Mitchell
J. Phys. B. **16**, L545, 1986.

24. Production of vibrationally cold ions using a radiofrequency storage ion source.
A. Sen and J.B.A. Mitchell
Rev. Sci. Instrum. **57**, 754,1986